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Charge Response Kernel Theory based on Ab Initio and Density Functional Calculations

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Abstract: The charge response kernel (CRK) of a molecule, $\partial Q_a/\partial V_b$, is formulated and calculated via *ab initio* molecular orbital and density functional theory, where Q_a is the partial charge of the site a and V_b is the electrostatic potential at the site b. The non-empirical definition of CRK provides a general and rigorous scheme of polarizable molecular modeling.

Keywords: charge response kernel, polarizability, density functional theory

1 Introduction

The electronic polarization is of vital importance in intermolecular interactions in condensed phases, in particular, to correctly describe solvation energetics and structures. Therefore, most molecular models in common use incorporate the electronic polarization effects in either implicit or explicit way. The former, implicit way employs a nonpolarizable molecular model with augmented polarization, such as the SPC [1] or TIP4P [2] water model, while the latter uses a polarizable molecular model. Although the latter is computationally more demanding than the former for use of molecular simulation, it is capable of describing both spatial and temporal fluctuation of molecular polarization, which often plays crucial roles in local solvation or interface structures [3, 4].

The charge response kernel (CRK) is considered as a general model to explicitly represent the molecular polarization [5]. It is defined as $(\partial Q_a/\partial V_b)_N$ on the basis of the interaction site representation, where Q_a is the partial charge at the site a and V_b is the electrostatic potential at the site b. This property is readily incorporated into the molecular dynamics simulation based on the interaction site molecular models, introducing fluctuating partial charges on the interaction sites.

We propose the *ab initio* formulation of the CRK, due to the following advantages. First, the *ab initio* theory obviates empirical parameterization to determine the CRK, and therefore it is generally applicable to any molecule by *ab initio* calculations. Second, the accuracy and reliability of the CRK are warranted by those of the underlying electronic structure theory at any level of accuracy. Third, these general features of the *ab initio* CRK provide an equal footing to treat the electronic polarization of solute and solvent molecules, including novel solute species that are often difficult to deal with by an empirical model. As one example, the CRK model in combination

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of molecular dynamics simulation was successfully utilized to elucidate the anomalous diffusion of some aromatic transient radicals in solutions [6].

In the present paper, first we briefly summarize the theoretical framework of the CRK model in the *ab initio* molecular orbital theory. Then we extend the formulation to the density functional theory, and demonstrate the accuracy of the calculated results.

2 Ab Initio Theory

In our theoretical treatment, the partial charge Q_a is defined as a electrostatic potential charge, which is optimized to reproduce the surrounding electric field generated by the molecule. The partial charge Q_a is given by an one-electron operator $\hat{Q}_a$ as $Q_a = \langle\Psi|\hat{Q}_a|\Psi\rangle$, where Ψ denotes the wavefunction of the many-electron system. The detailed form of $\hat{Q}_a$ is presented in our previous works [5].

The molecular Hamiltonian in the condensed phase, $\hat{H}$, is given by $\hat{H} = \hat{H}_0 + \hat{H}'$, where $\hat{H}_0$ is the molecular Hamiltonian in the gas-phase and $\hat{H}'$ is the perturbation Hamiltonian $\hat{H}'$ by the solvation environment. The latter, $\hat{H}'$, is given in the interaction site representation as

$$\hat{H}' = \sum_a^{\text{sites}} \hat{Q}_a V_a, \tag{1}$$

where V_a is the electrostatic potential at the site a generated by the ambient solvent.

The CRK $K_{ab} = (\partial Q_a/\partial V_b)$, by definition, is represented via the first derivative of the wavefunction Ψ^b with respect to the external electrostatic potential V_b at site b,

$$K_{ab} \equiv \frac{\partial Q_a}{\partial V_b} = \frac{\partial^2 E}{\partial V_a \partial V_b} = \langle\Psi^b|\hat{Q}_a|\Psi\rangle + \langle\Psi|\hat{Q}_a|\Psi^b\rangle. \tag{2}$$

Note that the CRK is equivalent to the second derivative of the total energy E. The derivative of the wavefunction is generally formulated by the coupled-perturbed Hartree-Fock equation in the *ab initio* theory [7]. We first illustrate this scheme in a simple case of the closed-shell Hartree-Fock theory.

Suppose the molecular orbital and its derivative by V_a are denoted by C_{pi} and C_{pi}^a. In the followings, suffixes p, q, ... refer to atomic orbital (AO), and i, j, ... to molecular orbital (MO). The derivative coefficient C_{pi}^a is expressed in the MO representation using the transformation matrix U,

$$C_{pi}^a = \sum_j^{\text{MO}} C_{pj} U_{ji}^a, \tag{3}$$

and U is formulated by the following coupled-perturbed Hartree-Fock equation,

$$(\epsilon_l - \epsilon_i) U_{li}^a + \sum_j^{\text{occ}} \sum_k^{\text{vir}} H_{likj}^{(MO)} U_{kj}^a = -Q_{a,li}^{(MO)}, \tag{4}$$

where j and k indicate the occupied and virtual MO's, respectively. ϵ_i is the orbital energy of the i-th canonical MO, and H is given with the two-electron integrals (in the MO representation) as

$$H_{likj} = 4(li|kj) - (lk|ij) - (lj|ik). \tag{5}$$

Eq. (4) is a set of linear equations for U, which derives the CRK as follows,

$$K_{ab} = \sum_i^{\text{occ}} \sum_j^{\text{vir}} 4 Q_{a,ij}^{(MO)} U_{ji}^b. \tag{6}$$

3 Density Functional Version

The density function theory (DFT) is in widespread use in the last decade in the field of quantum chemistry [8]. Its amazing success hinges on the exchange-correlation functionals developed to date, such as B3LYP [9, 10], which can take account of the electron correlation effects fairly accurately at a modest computational cost. Since the Kohn-Sham formalism is quite analogous to the Hartree-Fock formalism, the extension of the CRK model to the density functional theory is straightforward, as shown in the followings.

The Kohn-Sham matrix is represented as

$$F_{pq}^{\mathrm{KS}} = h_{pq} + \sum_{r,s} (pq|rs) D_{rs} + V_{pq}^{xc}[\rho], \tag{7}$$

where $V_{pq}^{xc}[\rho] = \delta E^{xc}[\rho]/\delta D_{pq}$ is the exchange-correlation potential, which is the derivative of the exchange-correlation energy functional $E^{xc}[\rho]$ with respect to the density matrix D_{pq}.

The formulation of the Kohn-Sham matrix, (7), coincides with that of the Fock matrix by replacing the exchange-correlation potential V_{pq}^{xc} with the exchange term, $-\sum_{r,s}(pr|qs)D_{rs}$. Accordingly, eq. (4) is modified in the DFT case by replacing H with the Kohn-Sham equivalent as,

$$H_{pqrs} \rightarrow 4(pq|rs) + \delta V_{pq}^{xc}/\delta D_{rs}. \tag{8}$$

The DFT version of eq. (4) is often called coupled-perturbed Kohn-Sham equation. Details for the second term are given in the general analytical second derivative of the density functional theory [11].

We calculated the CRK via the DFT and compared them to those by the Hartree-Fock case. Table 3 illustrates the results of NH_3. The program code for the CRK calculation was implemented into the GAMESS-UK package [12]. To evaluate the reliability of the calculated CRK, the electronic polarizability derived from the CRK is compared to the experimental value. The polarizability α_{ij} is derived from the CRK as

$$\alpha_{ij} = -\sum_{a,b}^{\text{sites}} \frac{\partial Q_a}{\partial V_b} \, r_i(a) \, r_j(b), \qquad i,j = x,y,z, \tag{9}$$

where $r_i(a)$ is the i-th Cartesian coordinate of the site a. The calculated CRK derives an isotropic polarizability of $\bar{\alpha} = 12.13$ a.u. (HF) and 13.59 a.u. (B3LYP), while the experimental value is 15.25 a.u. While both results are fairly consistent to the experiment, the density functional calculation shows some improvement in evaluating the electronic polarization. Computational cost of the CRK is almost equivalent to that of the analytical calculation of the conventional dipole polarizability.

Table 1: Charge Response Kernel of NH_3 molecule, calculated by (a) HF and (b) B3LYP. The basis set is d-aug-cc-pVTZ for N and aug-cc-pVTZ for H, with s and p diffusion functions only, (12s7p2d1f/6s3d1d) / [6s5p2d1f/4s3p1d]. Unit: a.u.

(a) HF

	1	2	3	4
1(N)	-23.98			
2(H)	7.99	-4.38		
3(H)	7.99	-1.81	-4.38	
4(H)	7.99	-1.81	-1.81	-4.38

(b) B3LYP

	1	2	3	4
1(N)	-28.39			
2(H)	9.46	-5.03		
3(H)	9.46	-2.22	-5.03	
4(H)	9.46	-2.22	-2.22	-5.03

4 Summary

In this work, the Charge Response Kernel ($\partial Q_a/\partial V_b$) formulated via the ab initio molecular orbital theory by us is extended to the density functional theory. These definitions of CRK rigorously based on the quantum chemical theories can provide a general scheme to construct polarizable molecular models. We plan to adopt this CRK model to molecular simulation of the interfacial nonlinear spectroscopy. Such work is now in progress in our group.

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[12] GAMESS-UK is a package of ab initio programs written by M.F. Guest, J.H. van Lenthe, J. Kendrick, K. Schoffel, and P. Sherwood, with contributions from R.D. Amos, R.J. Buenker, H.J.J. van Dam, M. Dupuis, N.C. Handy, I.H. Hillier, P.J. Knowles, V. Bonacic-Koutecky, W. von Niessen, R.J. Harrison, A.P. Rendell, V.R. Saunders, A.J. Stone, D.J. Tozer, and A.H. de Vries. The package is derived from the original GAMESS code due to M. Dupuis, D. Spangler and J. Wendoloski, NRCC Software Catalog, Vol. 1, Program No. QG01 (GAMESS), 1980.